# RAW MATERIALS. UTILIZATION OF WASTE

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## USE OF UNCONVENTIONAL RAW MATERIALS WITH REGARD TO THEIR REDOX PROPERTIES

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The possibility of using nontraditional materials allowing for their redox parameters in the production of container glass to replace sand and soda is investigated. It is established that the color and quality of glass can be predicted based on integrated use of such parameters as the chemical oxygen minimum and the redox potential of a batch.

The problem of expanding available raw materials for glass production is topical. It is interesting to use unconventional materials represented by industrial waste or by natural minerals. However, the use of such materials creates certain difficulties due to the necessity for their additional processing, homogenizing, and correction of glass batch formulas.

As a rule, raw materials in glass production are estimated based on their chemical and granulometric compositions. However, the redox characteristics of materials are significant as well and have to be taken into account when judging the suitability of a material for specific glass production.

It is known that fluctuations in the content of oxidizers and reducing agents in glass batches result in a shift of equilibrium between variable-valence oxides (primarily iron), which complicates the glass-melting process and has a negative effect on color stability [1].

Various aspects of the effect of redox parameters of materials on the melting specifics and tint of glass are extensively discussed in the literature. However, the use of these characteristics in solving the problem of replacing traditional materials by new ones is not sufficiently studied.

Batches were prepared that contained the traditional raw materials, such as sand, soda, dolomite, sulfate, and coke, and also the following materials:

sand $ST_2$ from the Tuganskoe deposit, which is a byproduct of zircon-ilmenite ore concentration, replaced sand $ST_1$ from the Tashlinskoe deposit;

natural soda (NS) from the Mikhailovskoe deposit, as well as the product of dehydration of sulfur-alkaline waste (SAW), which is waste of ethylene production generated at the Tomsk Chemical Works, replaced synthetic soda (SS).

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A specific feature of the quartz-bearing component in the sand from the Tuganskoe deposit is fine dispersion: particles sized below 0.2 mm constitute up to 65% (Table 1).

The chemical composition of sand from the Tuganskoe deposit is virtually no different from Tashlinskoe sand and belongs to the group of pure quartz sands, in which the content of colorant impurities ($TiO_2$, $Fe_2O_3$) and $Al_2O_3$ does not exceed the standard requirements (Table 2).

Natural soda used to replace synthesized soda ash was obtained by drying raw soda at a temperature of 350°C and subsequent milling to complete passage through a sieve with a hole size of 0.3 mm. The distinctions in the chemical composition of synthesized soda from natural soda involve a lower content of the main component ($Na_2CO_3$) and an increased content of sodium sulfate and impurities in the form

**TABLE 1**

| Sand | Weight content, %, of fraction | | | | | | |
|---|---|---|---|---|---|---|---|
| | above 0.5 | 0.5 – 0.315 | 0.315 – 0.25 | 0.25 – 0.2 | 0.2 – 0.16 | 0.16 – 0.1 | below 0.1 |
| $ST_1$ | 9.0 | 48.0 | 26.0 | 8.0 | 6.0 | 3.0 | – |
| $ST_2$ | – | 0.6 | 7.0 | 20.0 | 20.0 | 34.0 | 12.4 |

**TABLE 2**

| Sand | Weight content, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $Fe_2O_3$ | $TiO_2$ | calcination loss |
| $ST_1$ | 99.10 | 0.27 | 0.07 | 0.05 | 0.10 | – | 0.41 |
| $ST_2$ | 98.80 | 0.67 | 0.07 | 0.02 | 0.09 | 0.06 | 0.94 |



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**TABLE 3**

| Material | Weight content, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $Na_2CO_3$ | NaCl | $Na_2SO_4$ | NaOH | $Na_2S$ | $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ | calcination loss |
| SS | 99.31 | 0.37 | 0.02 | – | – | – | – | – | 0.30 |
| NS | 74.55 | 0.45 | 18.82 | – | – | 0.11 | 5.13 | 0.54 | 0.40 |
| SAW | 92.53 | 2.80 | 0.49 | 3.47 | 0.01 | – | – | – | 0.70 |

of $SiO_2$, $Al_2O_3$, and $Fe_2O_3$. However, it should be noted that $SiO_2$ and $Al_2O_3$ are glass-forming oxides and their presence can be allowed for in correcting the batch formula, whereas $Fe_2O_3$ may produce a modification of the glass tint.

The ethylene production waste was obtained by drying liquid waste at a temperature of 150°C and milling it to complete passage through a sieve with a hole size of 0.3 mm. The specific feature of this alkali material is an increased content of sodium hydroxide and sodium chloride, and also the presence of an oxidizer and a reducing components in the form of sodium sulfate and sulfide.

The chemical compositions of alkali-containing materials determined according to the state standard requirements are given in Table 3.

Model batches were prepared based on an industrial batch for container glass of the following composition (wt. %): 71.30 $SiO_2$, 14.60 $Na_2O$, 11.00 (CaO + MgO), 2.80 $Al_2O_3$, and 0.19 $Fe_2O_3$.

The redox state of a batch was estimated based on its chemical oxygen minimum (COM). This parameter was found by the bichromatometry method, i.e., oxidation of the reducing agents in batch materials by excess oxidizer and sunsequent titration of its residue [2].

The experimental values of COM of materials (Table 4) were used to calculate the COM of model batches using the following formula:

$$\mathrm{COM_b} = \frac{\sum \mathrm{COM}_i P_i}{\sum P_i},$$

where $\mathrm{COM}_i$ is the chemical oxygen minimum of the material, mg $O_2$ per 100 g; $P_i$ is the weight content of the material in the batch, %.

The COM of batch composition 1, 2, 3, 4, and 5 was equal to 57.17, 100.70, 131.90, 117.70, and 162.50 mg of $O_2$ per 100 g, respectively.

Some authors [3, 4] specify intervals of COM values typical for producing clear glass, which on the average is equal to 100 mg of $O_2$ per 100 g of batch, whereas production of semiwhite and green glass is possible with a COM within an interval of 100 – 250 mg $O_2$ per 100 g of batch.

It can be seen from the data in Table 4 that batches for semiwhite and green glasses based on nontraditional materials have higher values of COM than batches based on synthesized soda and sand from the Tashlinskoe deposit, but stay within the permissible value limits.

**TABLE 4**

| Material | COM, mg $O_2$ per 100 g | Weight content, %, in batch | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 |
| $ST_1$ | 55 | 59.32 | – | – | 61.39 | – |
| $ST_2$ | 128 | – | 59.71 | 57.74 | – | 61.43 |
| SS | 71 | 19.85 | 19.80 | – | – | – |
| NS | 161 | – | – | 22.68 | – | – |
| SAW | 385 | – | – | – | 19.39 | 19.39 |
| Dolomite | 46 | 18.13 | 18.07 | 17.89 | 18.14 | 18.10 |
| Alumina | 86 | 1.74 | 1.49 | 1.35 | 1.08 | 1.08 |
| Sulfate | 64 | 0.96 | 0.96 | – | – | – |
| Coke | 3760 | – | – | 0.32 | – | – |

**TABLE 5**

| Material | $F_i$ | Quantity of material in batch, kg, per 2000 kg of sand | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 |
| $Na_2SO_4$ | + 0.67 | 32.37 | 32.16 | 147.8 | 3.26 | 3.26 |
| $Na_2S$ | – 1.60 | – | – | – | 0.03 | 0.03 |
| Coke (85% C) | – 5.70 | – | – | 11.08 | – | – |

However, the described method for identifying the redox parameters of batches does not take into account the oxidizing effect of sulfates; therefore, the redox potential (ROP) of batches was identified as well as an additional characteristic. The ROP was calculated based on the formula [4]:

$$\mathrm{ROP} = \sum F_i P_i^1;$$

$$P_i^1 = \frac{2000 P_i}{P_s},$$

where $P_i^1$ is the weight of the $i$th component calculated per 2000 kg of sand; $F_i$ is the redox factor of the $i$th component of the batch; $P_s$ is the weight content of sand in the batch, %.

The calculation results are shown in Table 5.

The ROP of batch compositions 1, 2, 3, 4, and 5 is equal to 21.69, 21.54, 35.87, 2.13, and 2.13, respectively.

It follows from the above data that all model batches are oxidizing (positive ROP values), and iron is present in their melts in the form of $Fe^{3+}$ and $Fe^{2+}$ ions, which determines the production of glasses with various shades of green. The ROP values, according to various authors, for semiwhite (green) container glasses are within the limits from + 12 to – 20 [4, 5].

The ROP of batches makes it possible to predict not only the color of glasses but the behavior of batches in melting as well. It is known, for instance, that glasses melted from highly oxidizing batches in the case of the furnace atmosphere or temperature changing are prone to formation of seeds.

Comparative melting of glass based on traditional and model batches was carried out in a laboratory electric furnace with silit heaters in corundum crucibles of 1-liter capacity at a temperature of 1450°C with an exposure of 1 h. No significant differences were registered in the course of melting. The glass samples obtained had the following colors: compositions 1 and 2 — clear; composition 3 — light green shade; compositions 4 and 5 — yellow-green. Analysis of transmission spectra (spectrophotometer SF-26) of samples 0.5 – 0.7 mm thick in the spectrum range of 400 – 700 nm indicated that light transmission values of glass based on model batches are 2 – 4% lower than those of glasses melted from traditional materials, which is not significant for container glass.

Thus, an integrated use of redox characteristics makes it possible to predict the color and quality of glass to be obtained when traditional materials are replaced by new ones.

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